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## ABSTRACT (Maximum 200 words)

The study of molecular dication chemistry has concluded with a detailed study of the reactions of  $CF_n^{2+}$  with  $D_2$  and  $O_2$ , as well as with rare gases. A particularly surprising result was the detection of major channels of bond breaking and bond forming in reactions of dications with  $D_2$  and  $O_2$ . Other  $H_2CCC^-$  autodetachment studies aided our understanding of energy flow from vibration and rotation to electronic energy in reactive species. Experiments to study the properties of ionic chromophores in solvents have continued, and time-resolved dynamic studies have given clear evidence of solvent shell breakup. Related theoretical studies investigate the stability of ions in a solvent, treating the effect of the solvent as producing a strong electric field at the center of mass of the chromophore. Preliminary experiments showed the feasibility of trapping ions in  $O_2$  solvents.

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# **Theoretical/Experimental Investigations of Dications and Cluster Ions**

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## **I. Final Report of Dication and Cluster Ion Research**

Research supported in this program involved experimental and theoretical explorations of the stability and reactivity of doubly charged ions. Doubly charged molecular ions are novel species with unique energetic and bonding properties. As a class, they exhibit high energy content, long lifetimes against predissociation, and bonding partnerships for which there are no neutral analogs. A goal of this research was to understand the bonding of these species and their energy release in chemical transformations.

In the laboratory, molecular dications are prepared by electron impact ionization and are mass selected. For reactive studies, the beam of ions is crossed with a pulsed jet of neutral reactants and the ion products are detected with a time-of-flight mass spectrometer. The results of these studies have shown some remarkable properties and trends, which are important in determining their stability, as enumerated below. For spectroscopic studies, the ions are prepared in a beam and interrogated with laser beams, through the processes of high resolution predissociation spectroscopy and photofragmentation pathways. In the high resolution studies, the apparatus is a coaxial negative ion-laser beam spectrometer converted for positive ion studies, with product detection capabilities modified to enable the detection of ionic photofragments.

Theoretical investigations involve complete active space self consistent field (CAS-SCF) and multi-reference configuration interaction (MR-CI) techniques to investigate the stability of isolated dication species and to determine their reactivity with various collision partners. We have shown that the CAS-SCF theoretical methods are only qualitatively correct for dications. The MR-CI method combined with the insights from the CAS-SCF are essential for accurate predictions.

The theoretical program carried out a broad *ab initio* CAS-SCF survey of several classes of interesting diatomic dications and then selected several species for accurate MR-CI examination. The first row diatomic hydrides show little tendency to form quasi-bound dications. This may be because the spatially compact L-shell orbitals form a bond only at distances short enough to produce an insurmountable Coulomb repulsion of the constituent nuclei. One strong exception is

$\text{BeH}^{2+}$ , which exhibits a strong well in the  $^2\Sigma^+$  symmetry with the lowest vibrational level about three eV above the asymptote.

Perhaps because the greater spatial extent of the M-shell orbital permits bond formation at somewhat longer distances, the second row hydrides form quasi-bound dication readily, with  $\text{MgH}^{2+}$ ,  $\text{AlH}^{2+}$ ,  $\text{SiH}^{2+}$ ,  $\text{PH}^{2+}$ ,  $\text{SH}^{2+}$ , and  $\text{ClH}^{2+}$  developing wells deep enough to trap several vibrational levels. Detailed MR-CI studies and vibrational analyses were carried out on two of these species,  $\text{PH}^{2+}$  and  $\text{SH}^{2+}$ , the latter in parallel with laboratory measurements. One interesting trend is that even though hydrogen tunnels with impunity in more typical chemical systems, the lifetimes of the  $v=0$  levels in the quasi-bound dication are essentially infinite. The explanation rests partly with barrier height and partly with an atypical barrier width, the outer limb falling off only as  $1/R$  rather than the  $1/R^6$  appropriate to the potentials of most neutrals.

Exploratory state-averaged full valence CAS-SCF calculations on  $\text{CF}^{2+}$  including all doublet states arising from the  $^2\text{P}_u(\text{C}^+) + ^3\text{P}_g(\text{F}^+)$  asymptote showed the  $\text{X}^2\Sigma^+$  and  $\text{A}^2\Pi$  states possess deep quasi-bound potential wells, and reveal inflection points in the potential energy curves of the  $^2\Delta$ ,  $^2\Pi$ , and  $^1\Sigma^-$  states. The existence of another metastable doublet state correlating with the lowest asymptote cannot be ruled out from these calculations. However, as indicated by the CAS-SCF calculations such a state would lie at least 1.5 eV above the top of the barrier of the  $\text{X}^2\Sigma^+$  state. The quartet states were not considered in this work since their high spin is inauspicious for bonding. The MR-CI potential energy curves of the  $\text{X}^2\Sigma^+$  and  $\text{A}^2\Pi$  states were calculated at 18 internuclear distances between 1.6 and 10.0 Bohr. Beyond a distance of about 8 Bohr the potentials revert to a Coulomb repulsion between  $\text{C}^+$  and  $\text{F}^+$ . At bonding distances the situation is similar to the known  $\text{NO}^{2+}$ , with a shallow  $^2\Pi$  well lying above a much deeper  $^2\Sigma^+$  well. The electronic character at the well minima was consistent with  $\text{C}^{2+}-\text{F}$ . Preparation of  $\text{CF}^{2+}$  by a vertical double ionization from the neutral  $\text{CF}(\text{X}^2\Pi)$  molecule in  $v=0$  ( $R_e = 2.4$  Bohr) will produce predominantly  $\text{CF}^{2+}$  in the  $\text{X}^2\Sigma^+$  ground state with vibrational quanta of  $v=2$  and 3.

The high resolution laser spectroscopic studies were directed toward obtaining information on  $\text{N}_2^{2+}$  electron states and the subtle issues of dication stability. The investigations near  $15,000 \text{ cm}^{-1}$  showed a more complex spectrum, which under high resolution indicated over 350 individual lines in this region; this represents far too many lines to be a simple member of a previously reported band system. The detailed analysis of this spectrum was greatly aided by the electronic structure calculations. This work indicated the strong possibility of a  $^3\Pi - ^3\Sigma$  transition in the energy range that we observed. Computed bond lengths for the two states gave a very good starting point for recognizing a few progressions. The analysis gave an unequivocal confirmation of the assignment. All of the 27 rotational branches possible in such a transition were present in the spectrum and assigned. Of particular note is the fact that the spectroscopically analyzed triplet transition is between two excited states. The energy difference between the singlet and triplet states was determined by the accurate calculations, as were the overall potential energy curves.

The upper  $^3\Pi$  state of  $\text{N}_2^{2+}$  appears to support only one bound vibrational level, and the shape of the barrier potential is indicative of extensive configuration mixing. Such a state provides a particularly sensitive test of the ability to compute potentials and tunneling lifetimes. Since individual rotational lines are well resolved in the high resolution spectrum, it is possible to obtain lifetimes for this electronic state for various rotational levels. There is no striking

rotational dependence. The observed long lifetime of 50 ps is at variance with the initially calculated lifetime (1 ps), and indicates that unexpected additional states are producing an even larger barrier to dissociation. Finally, the high resolution ion spectrometer was converted from dication photodissociation studies to anion autodetachment in order to investigate the rates of energy flow in photoexcited anionic clusters. This capability was to provide a supplementary structural capability to the large cluster dynamics described in the following section. In the process of this conversion, Yokoyama has carried out a detailed study of energy flow in the very unstable  $\text{H}_2\text{C}=\text{C}=\text{C}^-$  ion. The neutral propadieneylidene molecule has a large permanent electric dipole moment, and can support a weakly bound electronically excited state. By studying the rate at which energy flows from vibrational and rotational degrees of freedom into the electronic degree of freedom, we have learned a great deal about processes which destabilize these reactive molecules. Two manuscripts describing this work are submitted and a third is in final preparation.

Detailed studies of reactivity were completed between  $\text{CO}^{2+}$ ,  $\text{COS}^{2+}$ ,  $\text{CO}_2^{2+}$ ,  $\text{CF}^{2+}$ ,  $\text{CF}_2^{2+}$ ,  $\text{CF}_3^{2+}$ ,  $\text{SF}_2^{2+}$ ,  $\text{SF}_3^{2+}$ , and  $\text{SF}_4^{2+}$  with each of the rare gases, between  $\text{CO}_2^{2+}$ ,  $\text{CF}^{2+}$ ,  $\text{CF}_2^{2+}$ ,  $\text{CF}_3^{2+}$ ,  $\text{SF}_2^{2+}$ ,  $\text{SF}_3^{2+}$ , and  $\text{SF}_4^{2+}$  with  $\text{D}_2$  and between  $\text{CF}^{2+}$  and  $\text{CF}_2^{2+}$  with  $\text{O}_2$ . The reactions are studied at low enough collision energies that chemical bond transformations are observed, as well as charge transfer, collision-induced dissociation and neutral loss channels. New studies will involve the reactions of dications with hydrocarbon molecules.

A number of important principals have been elucidated from the reaction studies. Experimentally, it is found that collision-induced dissociation (or predissociation) of the dications does occur, especially with the lighter rare gases such as He and Ne. However, the cross sections for these processes are typically small, less than  $1 \text{ \AA}^2$ . Charge transfer reactions have large cross sections, but charge transfer is restricted to those processes that are intrinsically exothermic, *i.e.* not including the collision energy. Essentially charge transfer does not occur if kinetic energy is required. This is explained by simple Landau Zener models of the collision process. In addition, the observed product states of charge transfer obey a rigorous Landau Zener formalism in which the potential curves must cross within an appropriate small range of distances in order for reaction to occur. Because of this mechanism, the reactions are remarkably specific in producing selected product species or states. The MR-CI calculations for  $\text{CO}^{2+}$  with Ne confirm this analysis. We have also observed a first example of a double charge transfer process with a molecular dication in the reaction of  $\text{CO}^{2+}$  with Xe.

Surprisingly, we also detect major channels of bond breaking and forming in reactions of dication species with  $\text{D}_2$  and  $\text{O}_2$ . For example, the reaction of  $\text{CF}_2^{2+}$  with  $\text{D}_2$  forms  $\text{DCF}_2^+$  in high yield, effectively competing with charge transfer, and the reaction of  $\text{CO}_2^{2+}$  with  $\text{D}_2$  forms  $\text{DCO}^+$  as one of the highest yield ion products. These results are surprising in light of the large charge transfer cross sections which are available in these systems. Evidently, the dications are able to get close enough together to induce chemical bond transformations, without immediate predissociation or charge transfer followed by separation of products. The evidence for neutral loss reactions and chemical bond breaking and forming represent general new classes of reactions involving multiply charged ions.

It was found that these ions react rapidly with all types of collision partners, thus indicating that it is unlikely that they can be trapped and used for energy storage. An important result was uncovered, which suggests a concept of stable "core" dication species. For example, in the collisions of a species such as  $\text{CF}_3^{2+}$  with rare gases, a neutral loss channel occurs to form  $\text{CF}_2^{2+}$

+ F, and this is found to be a very dominant mechanism. Subsequent theoretical calculations confirmed that the  $\text{CF}_2^{2+}$  dication, which is isoelectronic with  $\text{CO}_2$ , has 1.06(+) positive charge on the C atom with 0.47(+) on each of the F atoms. The  $\text{CF}_2^{2+}$  ion apparently forms a weaker, inequivalent bond to third F atom. The core ion principle was subsequently also demonstrated for  $\text{SF}_4^{2+}$  and  $\text{SF}_3^{2+}$ , which produce, for example,  $\text{SF}_2^{2+}$  readily upon collisions.

Expecting that the core ion idea may be an important general principle, we initiated experiments to photodissociate  $\text{CF}_3^{2+}$  and  $\text{SF}_4^{2+}$  with a pulsed laser. We found, indeed, that  $\text{CF}_3^{2+}$  dissociates with high probability to form  $\text{CF}_2^{2+}$  and neutral F atom. This occurs from 600 nm in the visible to 1060 in the near infrared, as well as at 532 and 355 nm, without any discernible structure. This exciting result suggests that there is at least one low-lying electronic transition in this ion which leads by a low energy pathway to dissociation to neutral F. Studies of  $\text{SF}_4^{2+}$  photofragmentation showed no product ions over the range of wavelengths tested, but collisional studies indicated that higher energies are required to produce the neutral F atoms. We believe that these results indicate the absence of low-lying electronic transitions in this ion.

Subsequent studies also explored the reactions and photofragment products of a whole series of  $\text{SiF}_x^{2+}$  and  $\text{CCl}_x^{2+}$  ions. One very exciting discovery is that the ion  $\text{SiF}^{2+}$  dissociates both upon collisions and with photo-excitation to produce  $\text{Si}^{2+}$ . Calculations indicate that the electronic structure of  $\text{SiF}^{2+}$  has 2.25(+) charge on the Si and 0.25(-) charge on the F atom. Thus the collisional and photodissociation pathways reveal the predominant electronic structure in the dication. A large series of studies on the  $\text{SiF}_x^{2+}$  reactions and photofragmentation have also now been completed.

In a further study, the  $\text{CCl}_3^{2+}$  ion was examined for both reactive collisions and photofragmentation. Photolysis of  $\text{CCl}_3^{2+}$  at 1064 nm results in  $\text{CCl}_2^{2+}$ ,  $\text{CCl}_2^+$ , and  $\text{Cl}^+$ . When the laser is tuned to shorter wavelengths, in the visible, the  $\text{CCl}^+$  fragment is also produced. The threshold for photoproduction of  $\text{CCl}^+$  is 2.2 eV. However, when Ne is used as a collision partner, a much higher center-of-mass collision energy of 7-9 eV is required to produce  $\text{CCl}^+$ , suggesting that different excited states may be involved in the collisional and photodissociative processes.

## II. Ultrafast Cluster Dynamics

The experimental apparatus to study dynamics in size-selected ionic clusters is basically a supersonic expansion electron impact ionization ion source, coupled with tandem time-of-flight mass spectrometers. Ionic chromophores are formed by electron attachment near the orifice of a pulsed supersonic expansion, and the charged chromophore acquires a solvent shell as it drifts in the cold expanding gas. Depending upon expansion conditions, the chromophore can attach anywhere from 1 to 50 or more solvent molecules. A pulsed electric field extracts the cluster ions into a tandem time-of-flight mass spectrometer. Ultrafast pump-probe laser pulses interact with selected ions at the spatial focus of the first time-of-flight spectrometer. The ionic photoabsorption products are mass analyzed in the reflectron, and detected at the second spatial focus. The primary emphasis was placed upon an  $\text{I}_2^-$  chromophore contained in a  $\text{CO}_2$  solvent shell, with 16  $\text{CO}_2$  molecules required to close the first solvent shell. The pump laser pulse photodissociates the  $\text{I}_2^-$ , while the second probe pulse monitors the breakup of the solvent cage or the possible cage recombination of the photodissociated chromophore.

The first key experimental result demonstrated 100% recombination probability for 700 nm-irradiated  $I_2^-$  whenever the ion was surrounded by a complete solvent shell. Such stability is not observed for  $I_2$  in liquids, emphasizing the importance of embedding HEDM additives in solid matrices to achieve maximal stability! The next issue concerns how rapidly the energy from the recombined  $I_2^-$  disperses into the solvent. When the recombination probability is 100%, the time in which the photon energy is degraded to the solvent is quite rapid. While the absorption recovery takes about 40 ps, the vast majority of the photon energy has been transferred to the solvent in  $\sim 10$  ps. While the  $I_2^-$  system was not of HEDM relevance, it afforded the opportunity to observe directly many of the important physical processes on a time scale appropriate for our experimental resolution (200 fs). Recent studies have demonstrated the ability to carry out similar investigations with odd oxygen cluster ions, and with an ionic chromophore embedded in an  $O_2$  cluster. Thus while the following conclusions are based on the  $I_2^-$  studies, they are much more general than the specific context.

In order to simulate the photodissociation and recombination process, electronic charge switching on the  $I_2^-$  ion must be taken into account. When the iodine nuclei are close together, charge will be spread out over the molecule, but as the nuclei separate during photodissociation it becomes localized on one atom or the other. As the molecule dissociates inside the cluster, the charge localizes on one atom and the solvent reorganizes itself into a configuration that stabilizes the localized charge; at the same time, however, it is the growing asymmetry of the solvent that allows the charge to localize in the first place. It is necessary, therefore, to allow the charge distribution to depend upon an effective solvent coordinate. Parson chose as the solvent coordinate the **electric field** that the solvent exerts on the embedded molecular ion. *Ab-initio* calculations of the electronic structure of  $I_2^-$  in a static field were used to develop a charge-switching surface that reflects this process, and this essential physics has been incorporated into an efficient molecular dynamics program.

An important conclusion derived from this model was that the simple mechanical picture of "caging", in which the solvent merely keeps the solute nuclei from flying apart, is seriously oversimplified. One must also take into account the effects of the solvent on the *electronic* states of the solute. This will be true not just for ionic solutes, but also for any system in which electronic excitation leads to substantial charge redistribution.

The  $I_2^- \cdot (CO_2)_n$  experiments raised many more questions than they answer. Most of them center around the nature of the relaxation processes reflected in the absorption recovery, the role of the solvent, and the dynamics of electron localization/delocalization as the ionic chromophore dissociates and subsequently recombines. The greatest difficulty in interpreting recombination dynamics with partially solvated  $I_2^-$  arises from the molecular symmetry and the inability to control which of the two heavy atoms remains charged following photodissociation. Much of this ambiguity can be eliminated by the study of  $ICl^-$ , because the solvent will initially cluster around the smaller chloride end of the molecule. By choosing the color of the photodissociating light, one can excite the partially solvated ion to states leading either to  $I^-$  product or  $Cl^-$  product. Initial studies of  $ICl^- (CO_2)_{2.5}$  have provided clear evidence of the importance of solvent reorganization following photoexcitation. Studies of this important system are continuing, and the role of the solvent structure on the dissociation dynamics is being investigated by Lineberger.

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